

Chemical Interactions Between Heavy Solvent Components and Coal During Coal Liquefaction

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Introduction

Interest in the heavy components in recycle solvents from direct coal liquefaction processes was generated when Kerr-McGee and Conoco reported that the addition of light SRC, a fraction from the critical solvent deashing step in the SRC Process, to the recycle solvent greatly improved overall solvent quality.⁽¹⁾ However, some heavy components are not beneficial and can lead to coke formation. Clearly, recycling some high molecular weight solvent components is beneficial to direct coal liquefaction processes while recycling others is not. The objective of this study has been to look at the chemical reactions of the heavier materials from an actual recycle solvent during the dissolving step of two-stage coal liquefaction.

Experimental Approach

The experimental approach has been to (1) obtain a recycle solvent from the Lummus integrated two-stage liquefaction (ITSL) process pilot plant, (2) distill the solvent to 454°C, (3) separate each distillation cut into fractions of chemically similar compounds, (4) characterize the separated fractions in detail, and (5) study the effects on liquefaction when each solvent fraction is used as a heavy recycle solvent additive in a microautoclave liquefaction experiment.

Coal and Solvent

Illinois #6 bituminous coal (Burning Star) which had been ground to 80 percent -200 mesh and dried to 4 percent moisture for use in the Lummus ITSL pilot plant was used for this work. An analysis is shown in Table 1. This coal was ground in Alabama and shipped to New Jersey so it may have experienced some oxidation, but it is probably typical of the coals which would actually be used in direct liquefaction processes. The coal was stored under nitrogen in glass jars after it was received in an attempt to minimize additional oxidation during storage.

Recycle solvent from the Lummus ITSL pilot plant was used as the solvent. This solvent is a +343°C distillation residue which had been partially hydrogenated in the process. The recycle solvent was distilled under vacuum to 427°C and a -427°C distillate and a +427°C residue were obtained and analyzed. Analysis of the starting recycle solvent and the two distillation fractions are listed in Table 2. Of the total solvent, 36 percent boiled below 427°C and 64 percent boiled above 427°C. The residue contained most of the heteroatoms; 80 percent of the nitrogen, 84 percent of the sulfur and 76 percent of the oxygen.

Solvent Separation

Separations of the solvent fractions obtained by distillation to 454°C were carried out as shown in Figure 1 using a column chromatography method developed by Later and Lee⁽²⁾. The sample (10 g) was coated on Brockman Activity 1 neutral alumina (200 g) and eluted with hexane, benzene, chloroform, and tetrahydrofuran. The chemical types eluted were non-aromatic hydrocarbons, aromatic hydrocarbons, N-aromatics, and O-aromatics, respectively. Some polar material was retained on the column.

TABLE 1. ANALYSES OF ILLINOIS #6 COAL FROM THE LUMMUS ITSL PROCESS PILOT PLANT

Proximate Analyses, Wt %	As-Received	Dry
Moisture	3.99	-
Ash	9.72	10.12
Elemental Analyses, Wt %		
Carbon	69.73	72.63
Hydrogen	4.93	4.67
Nitrogen	1.18	1.23
Sulfur	2.88	3.00
Oxygen (by difference)		8.35
H/C		0.77
Particle Size Distribution, Wt %		
+70 mesh	0.07	
-70 +120	3.64	
-120 +200	18.90	
-200 +325	14.84	
-325	62.55	

TABLE 2. ANALYSES OF RECYCLE SOLVENT FROM THE LUMMUS ITSL PROCESS PILOT PLANT

Sample	SCT Recycle Solvent (2SCT16-1122)		-427°C	+427°C	
Elemental Analyses, Wt %	MAF			MAF	
Ash	1.30	-	<0.01	2.00	-
Carbon	86.77	87.91	90.96	87.88	89.67
Hydrogen	6.88	6.97	7.12	6.18	6.31
Nitrogen	0.94	0.95	0.57	1.30	1.33
Sulfur	0.53	0.54	0.23	0.69	0.70
Oxygen (by difference)	3.6	3.63	1.12	1.95	1.99
H/C	0.95		0.94	0.84	
Distillation Data, Wt %					
-427°C	35.6				
+427°C	64.4				
Molecular Weight, g/mole	477		257	456	

A second separation was carried out on partially deactivated silicic acid (3 g water/100 g silicic acid) by coating it with the N-aromatic fraction (3.35 g) and eluting with carbon tetrachloride, benzene and tetrahydrofuran. These single solvents were used instead of the two-component solvents described by Later and Lee(2) so that they could be recycled in the large scale column chromatography equipment. Only the +454 C N-aromatic fraction was separated on silicic acid.

The results of the first column chromatography separation are shown in Figure 2. Of the -454 C fraction, 9.6 percent is non-aromatic hydrocarbons, 72.9 percent is aromatic hydrocarbons, 5.6 percent is N-aromatics and 0.4 percent is O-aromatics. Only 3.8 percent is polar material which did not elute from the column. Overall, 82.5 percent of the -454°C solvent fraction are heteroatom-free hydrocarbons. The +454°C fraction consists of only 1.3 percent non-aromatic hydrocarbons, 27.0 percent aromatic hydrocarbons, 4.8 percent N-aromatics and 33.3 percent O-aromatics. A large amount of polar material, 29.1 percent, is also present and does not elute from the column. The heteroatom-free hydrocarbons total only 28.3 percent of the +454°C recycle solvent fraction.

Several separations of the +454°C N-aromatic fraction on silicic acid gave yields of 13-26 percent primary nitrogen compound (aromatic amines), probably contaminated with tertiary nitrogen compounds in which the basic nitrogen is sterically "protected". The yield of acidic secondary nitrogen compounds (pyrroles, etc.) was 20-30 percent and the yield of basic tertiary nitrogen compound (pyridine derivatives) was 30-45 percent. Total recoveries ranged from 75-85 percent.

Results and Discussion

The separated fractions were characterized by measuring molecular weight (by Vapor Phase Osmometry using THF as the solvent), elemental analyses and $^1\text{H-NMR}$. This data was used to obtain average structural parameters by application of the Brown-Ladner equations.(3) Titrations of basic nitrogen were done using perchloric acid in acetic acid.(4) Titrations of acidic hydrogen were done by refluxing with metallic sodium in tetrahydrofuran, adding water after removing excess sodium, and back titrating the sodium hydroxide formed with standard HCl.(5) The analytical results are summarized in Table 3.

All of the coal liquefaction experiments were done in a microautoclave liquefaction apparatus using 5 minutes reaction time at 427°C under 1000 psi hydrogen (room temperature) with a solvent/coal/additive ratio of 2:1:0.5.

A diagram of the microautoclave reactor is shown in Figure 3. It consists of a 3/4-inch union-tee microreactor which has a volume of 22.4 cc, a valve to add and release gases, a thermocouple which extends into the microautoclave to monitor temperature, and a pressure transducer to monitor pressure during each experiment. The microautoclave is heated in a sand bath and shaken horizontally. A 3/8-inch ball bearing is added to facilitate mixing.

The product gases were analyzed by GC and the liquids and solids were fractionated by their solubilities in THF, toluene and heptane into insoluble organic material (IOM) plus ash, preasphaltenes, asphaltenes and oils. Yields were calculated and a complete mass balance was done for each experiment. Mass balances averaged 99.2 percent, excluding water and gases.

Non-Aromatic Hydrocarbons

The non-aromatic hydrocarbon fractions are complex mixtures of paraffins, olefins and naphthenes. The -454°C fraction has an average molecular formula of $\text{C}_{21}\text{H}_{32}$ (5 unsaturations or rings) and the +454°C fraction has an average molecular formula of $\text{C}_{26}\text{H}_{45}$ (3.5 unsaturations or rings). Comparison of the conversions to THF solubles (Table 4) shows that the heavier fraction is a better solvent. The non-aromatic hydrocarbons are expected to act only as a physical solvent since they contain few or no hydroaromatics which can lose hydrogen readily. The heavier material therefore appears to be better able to dissolve the products of liquefaction, possibly because more of the heavier fraction is in the liquid state and less in the vapor phase due to the higher boiling point range.

TABLE 3. ANALYSES OF -454 C AND +454 C RECYCLE SOLVENT FRACTIONS SEPARATED BY COLUMN CHROMATOGRAPHY

Fraction Temp Solvent	Non-aromatic Hydrocarbons -454 C, +454 C Pentane			Aromatic Hydrocarbons -454 C, +454 C Benzene		N-Aromatics -454 C, +454 C Chloroform		+454 C N-Aromatic Fractions Secondary-N Carbon tetrachloride		Primary-N Benzene		Tertiary-N Chloroform		OH-Aromatics -454 C, +454 C THF/Ethanol	
	Elemental Analyses, wt % HAF														
Carbon	88.03	87.26	92.40	93.18	86.30	87.14	88.83	88.12	86.89	88.12	86.89	88.12	86.89	76.50	73.02
Hydrogen	10.97	12.70	7.59	6.58	6.82	6.51	7.05	6.33	7.05	6.33	7.05	6.33	7.05	7.20	7.21
Nitrogen	0.00	0.00	0.00	0.00	4.11	2.77	1.64	2.03	1.86	2.03	1.86	2.03	1.86	1.37	1.37
Sulfur	0.00	0.00	0.00	0.00	0.58	1.51	0.18	0.58	0.18	0.58	0.18	0.58	0.18	0.58	0.58
Oxygen (diff.)	0.00	0.00	0.00	0.00	1.89	3.31	2.19	2.58	2.56	2.58	2.56	2.58	2.56	13.42	17.82
H/C	1.48	1.75	0.99	0.84	0.95	0.90	0.95	0.86	0.97	0.86	0.97	0.86	0.97	1.13	1.18
Molecular Weight, g/mole	289	352	247	300	230	347	398	381	396	381	396	381	396	217	325
Hydrogen Distribution, % of Total Hydrogen															
Aliphatic	74.2	100.0	31.0	25.9	20.4	23.3	34.8	31.1	26.9	31.1	26.9	31.1	26.9	28.2	24.1
Aliphatic α to aromatic	22.0	0.0	41.0	35.4	42.5	30.8	26.2	29.8	35.0	29.8	35.0	29.8	35.0	45.5	54.4
Aromatic (1)	3.8	0.0	28.0	38.7	37.0	44.7	36.8	38.3	35.3	38.3	35.3	38.3	35.3	25.9	20.0
Phenolic (2)	0.0	0.0	0.0	0.0	0	1.3	0.21	.76	2.9	.76	2.9	.76	2.9	1.8	1.5
Donatable H, wt % of Sample	-	-	1.52	1.42	1.43	0.88	1.31	0.93	1.17	0.93	1.17	0.93	1.17	1.53	1.77
Structural Parameters (4)															
f_a - aromaticity	0.29	-	0.65	0.74	0.70	0.76	0.70	0.77	0.70	0.77	0.70	0.77	0.70	0.58	0.54
R_A - number of aromatic rings	-	-	2.6	4.1	2.1	3.6	3.8	4.7	3.7	4.7	3.7	4.7	3.7	0.48	0.84
R_{A}/C_{Aro} - substitutable aromatic	-	-	0.74	0.65	0.1	0.73	0.72	0.64	0.73	0.64	0.73	0.64	0.73	1.	1.
edge atoms/total aromatic atoms	-	-	0.42	0.31	0.38	0.30	0.30	0.32	0.38	0.32	0.38	0.32	0.38	0.59	0.70
α - fraction aromatic edge atoms	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C_A - total no. aromatic C atoms	-	-	12.3	17.2	11.6	19.0	20.6	20.7	20.1	20.7	20.1	20.7	20.1	8.0	10.5
R_C - substituted aromatic C atoms	-	-	3.9	3.5	3.6	4.2	4.4	4.2	3.6	4.2	3.6	4.2	3.6	4.7	7.3
R_C - carbon atoms/saturated sub-	-	-	1.8	1.7	1.5	1.8	2.2	2.0	1.8	2.0	1.8	2.0	1.8	1.6	1.5
stituent	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Molecular Formula															
C	21	26	19	23	17	25	29	28	29	28	29	28	29	14	20
H	32	45	19	20	16	23	28	24	28	24	28	24	28	16	23
N	-	-	-	-	0	0	0.5	0.7	0.6	0.7	0.6	0.7	0.6	0.5	0.5
S	-	-	-	-	0.04	0.06	0.04	0.05	0.03	0.05	0.03	0.05	0.03	0.07	0.06
O	-	-	-	-	0.3	0.7	0.2	0.6	0.7	0.6	0.7	0.6	0.7	1.8	3.6
Nitrogen types, wt % HAF															
Basic nitrogen	-	-	-	-	2.08	0.84	0.09	0.52	1.58	0.52	1.58	0.52	1.58	0.69	0.54
Non-basic nitrogen (diff.)	-	-	-	-	2.33	1.63	1.55	2.01	0.45	2.01	0.45	2.01	0.45	1.17	0.83
Oxygen types, wt % HAF															
Acidic oxygen	-	-	-	-	-	1.35	0.24	0.77	3.27	0.77	3.27	0.77	3.27	2.07	1.73
Non-acidic oxygen (diff.)	-	-	-	-	-	1.89	1.95	1.81	0.31	1.81	0.31	1.81	0.31	11.35	16.09

- (1) Corrected for phenolic hydrogen
- (2) Assumes all acidic hydrogen is phenolic
- (3) Measured by titration of NaOH from refluxing in Na/THF followed by addition of H_2O
- (4) From application of Brown-Ladner parameters to NMR data
- (5) Aliphatics contaminated with some aromatics

Aromatic Hydrocarbons

The molecular formulas are $C_{19}H_{19}$ for the -454°C material and $C_{23}H_{20}$ for the $+454^{\circ}\text{C}$ fraction. The aromaticities (f_a) are 0.65 and 0.74 for the two fractions. These are hydrogenated materials and there are significant amounts of aliphatic rings (hydroaromatics) present. The molecular weights of the two fractions differ by only 53 g/mole.

Comparison of the liquefaction results (Table 4) shows that the lower boiling range fraction is the better solvent. The major reaction of these fractions is expected to be hydrogen transfer. The -454°C fraction has a higher H/C ratio (0.99 vs 0.84), is less aromatic (f_a 0.65 vs 0.74) and contains more hydroaromatic hydrogens (1.52 vs 1.42 wt %), as measured by assigning portions of the H^1 -NMR spectrum to hydrogens in cyclic structures α and β to an aromatic ring. Another factor, which has not been measured, is molecular size, which may also have an impact on the relative ability of the smaller and larger molecules to get close enough to the dissolving coal to transfer hydrogen. Only the larger size and boiling point of the $+454^{\circ}\text{C}$ molecules, which should make those molecules more able to physically support the dissolving coal, favor the heavier material.

N-Containing Aromatics

The difference in molecular weight between the N-aromatic fractions is large, 117 g/mole. The molecular formula of the $+454^{\circ}\text{C}$ fraction indicates that there is also one atom of oxygen present in each molecule. These fractions are polar but are also made up of condensed hydroaromatic structures, so they should be able to act both as hydrogen donors and as physical solvents. The H/C ratios are similar for the -454°C and $+454^{\circ}\text{C}$ fractions, 0.95 and 0.90 respectively, but estimation of donatable hydrogen by H^1 -NMR⁽⁶⁾ indicates that the lighter fraction should be a much better hydrogen donor, 1.43 weight percent donatable hydrogen vs 0.88 for the $+454^{\circ}\text{C}$ fraction.

The differences in hetero atoms types between the -454°C and $+454^{\circ}\text{C}$ fractions are significant. All of the oxygen in the -454°C fraction is non-acidic while only about 60 percent of the oxygen in the $+454^{\circ}\text{C}$ fraction is non-acidic. Of the nitrogen in the -454°C fraction 47 percent is basic (tertiary) but only 34 percent is basic in the $+454^{\circ}\text{C}$ fraction. The N/C mole ratio is also twice as large (.041 vs .024) in the lighter fraction.

The liquefaction results are compared in Table 4. Both N-aromatic solvent additives result in lower conversions, although the -454°C material is by far the more effective solvent. The hydrogen donation potential of the lighter N-aromatic fraction may be able to overcome most of the negative reactions which occur as a result of the increased polarity of the N-aromatics, compared to the aromatic hydrocarbons. A major reaction of these fractions is adduction of solvent to the dissolving coal to produce large yields of asphaltenes. This is also more pronounced in the $+454^{\circ}\text{C}$ fraction and may be due to the higher amount of acidic (phenolic) oxygen.

Primary, Secondary and Tertiary $+454^{\circ}\text{C}$ N-Aromatics

The $+454^{\circ}\text{C}$ aromatic fraction was split into three fractions by nitrogen type, as shown below:




<u>N-Type</u>	<u>Primary</u>	<u>Secondary</u>	<u>Tertiary</u>
Compound Type			
% of Total N			
Basic	24	5	78
Non-basic (diff.)	76	95	22
% of Total O			
Acidic	30	11	100
Non-acidic (diff.)	70	89	0

TABLE 4. COMPARISON OF EFFECTS OF -454 C AND +454 C SOLVENT FRACTIONS ON COAL LIQUEFACTION
(427 C, 5 min, 1000 psi (cold) hydrogen, 3 g Illinois #6 coal, 6.0 g -454 C
recycle solvent, 1.5 g solvent fraction)

Added Solvent Fraction	Temp. °C	Net Change (MAF basis) % of MAF Coal			Hydrogen Balance
		THF Insolubles	Preasphaltenes	Asphaltenes	Oils
None	-	-80.4	34.3	13.7	20.5
Aliphatic	-454	-81.2	33.3	33.7	5.4
Hydrocarbons	+454	-84.1	27.9	35.0	-2.8
Aromatic	-454	-87.6	33.1	27.2	15.5
Hydrocarbons	+454	-83.4	33.8	28.9	9.4
N-Containing	-454	-79.5	25.6	40.6	7.3
Aromatics	+454	-67.1	30.3	47.6	-6.4
Primary Nitrogen Aromatic	+454	-79.5 (1)	29.4	42.0	-8.2
Secondary Nitrogen Aromatic	+454	-81.0 (1)	29.8	28.8	-15.2
Tertiary Nitrogen Aromatic	+454	-71.7 (1)	19.7	48.6	-14.0
O-Containing	-454	(-58.3) (2)	24.6	38.9	-18.1
Aromatics	+454	-71.1	30.8	26.9	0.6

(1) All N-aromatic fraction data are based on single liquefaction experiments

(2) Incomplete THF insolubles recovery

The purity of nitrogen types in each fraction can be estimated from the ratios of basic to nonbasic nitrogen present. The primary nitrogen fraction is expected to be contaminated with significant amounts of tertiary nitrogen compounds in which the nitrogen is sterically protected⁽²⁾. About 24 percent of the nitrogen in this fraction is basic (tertiary) and the other 76 percent is assumed to be the desired primary nitrogen compounds. The secondary (acidic) nitrogen fraction is expected to be the most pure and it is 95 percent nonbasic nitrogen. The tertiary (basic) nitrogen fraction is 78 percent basic nitrogen.

Acidic (phenolic) oxygen is associated primarily with the basic nitrogen, probably in hydrogen bonds. The oxygen associated with secondary (acidic) nitrogen is primarily non-acidic, possibly substituted furans, also in hydrogen bonds. The same oxygen-nitrogen pairs also appear to be present in the contaminated primary nitrogen fraction. Although the primary nitrogen is neutral it should also be able to form hydrogen bonds with non-acidic oxygen.

All of the individual N-aromatic fractions are better solvents than the combined N-aromatics fraction as shown in Table 4. The tertiary nitrogen N-aromatics give the lowest conversions of the three fractions and the most asphaltenes. Based on net hydrogen used, the tertiary nitrogen compounds do not shuttle hydrogen. They may strongly bond with solvent and dissolving coal.

The secondary N-aromatics give the highest conversions and significantly lower asphaltene yields. They result in the largest net loss of oil which indicates that they are also adducted to the dissolving coal and solvent. They show some indication of shuttling hydrogen.

Although the nitrogen compounds have been reported to be good solvents for coal liquefaction, particularly if they are present when the coal moisture is released during drying and can replace the moisture in the coal pores before liquefaction temperatures are reached⁽⁷⁾, under the conditions used in these experiments they are relatively poor liquefaction solvents, particularly the tertiary-N fraction.

O-Containing Aromatics

The final fraction studied is an oxygen-containing aromatic fraction which eluted from the column chromatography separation. Although much of the oxygen in the coal liquefaction solvents is probably phenolic, titration of acidic hydrogen showed that 90-96 percent of the oxygen on the molecules that eluted was non-acidic, probably in functional groups such as substituted benzofurans. These materials have lower aromaticities than the other fractions and are highly substituted. The -454°C fraction contains an average of 2 oxygens per molecule and the +454°C fraction contains an average of 4 oxygens per molecule. The H/C ratios are high, 1.13 and 1.18, respectively, as are the weight percentages of donatable hydrogen, 1.53 and 1.77, respectively, however, as shown in Table 4, these fractions are very poor solvents. Apparently, the major reaction of this class of compounds is not hydrogen transfer. This may be because the "donatable" hydrogens are not really hydro-aromatic but are α to oxygen atoms. They seem to adduct in large amounts to solvent, as shown by the negative oil yields. They apparently are also poor physical solvents, possibly due to their low aromaticities and relatively large steric size, caused by the large number of substituents.

Conclusions

The hydrocarbon fractions in the recycle solvent have a positive effect on liquefaction while the heteroatom containing fractions have a negative effect. Since the combined amount of non-aromatic and aromatic hydrocarbons is about 82.5 weight percent of the -454°C recycle solvent and only 28.3 weight percent of the +454°C recycle solvent, it is not surprising that the overall effect of adding more -454°C solvent is positive and the overall effect of adding more +454°C solvent is negative (Table 5).

Among the opposing properties of higher molecules weight solvent components which can affect their efficiency as liquefaction solvents are improved

TABLE 5. COMPARISON OF EFFECTS OF +454°C AND -454°C RECYCLE SOLVENTS ON COAL LIQUEFACTION (427°C 5 min, 1000 psi (room temperature) hydrogen, 3 g Illinois #6 coal, 6 g -454°C recycle solvent)

Added Solvent Fraction	Total Solvent/Coal	Net Change (MAF basis), % of MAF Coal (1)			
		THF Insolubles	Preasphaltenes ⁽²⁾	Asphaltenes ⁽³⁾	Oils ⁽⁴⁾ Hydrogen Balance
None	2.0:1	-80.4	34.3	13.7	20.5 - .12
-454°C/1.5	2.5:1	-86.1	42.9	25.3	19.5 - .063
+454°C/1.5	2.5:1	-77.2	29.2	34.6	12.4 - .36

(1) Net change = $\frac{\text{Final weight (MAF)} - \text{Initial weight coal + solvent (MAF)}}{\text{WT MAF coal}} \times 100$
Initial weights measured by extraction

(2) Preasphaltenes = THF soluble-toluene insolubles

(3) Asphaltenes = Toluene soluble-heptane insolubles

(4) Oils = Heptane solubles

facility for hydrogenation reactions, but lower amount of donatable hydrogen present, lower vapor pressure at elevated temperature but the possibility that their increased size has a negative steric effect on their ability to transfer hydrogen. Comparisons of solvent fractions of differing molecular weights gives mixed results. Of the solvent components which are expected to react primarily by H-transfer (N-aromatics and aromatic hydrocarbons) the heavier fractions are less effective, possibly because of steric hindrance to hydrogen transfer and less available hydrogen to transfer, but of the solvent components expected to act only as physical solvents (non-aromatic hydrocarbons and O-containing aromatics) the heavier components are more effective than the corresponding lower molecular weight fractions.

There appears to be a relationship between the type of heteroatoms present in the recycle solvent fraction which is based on hydrogen bonding. These relationships appear to be an area where additional research may increase understanding of the weak bonds which are made and broken during liquefaction which result in net solvent loss and improved coal solubility. Another area where further research is needed is on the effect of steric size of the solvent components on coal liquefaction.

The overall effect of recycling heavy ends in the ITSL process is positive because it results in the production of a single, higher-value liquid product with low carcinogenicity, in higher yields than would otherwise be possible. The hydrocarbons, about 25 percent of the heavy ends, are productive liquefaction solvent components as well.

Acknowledgements

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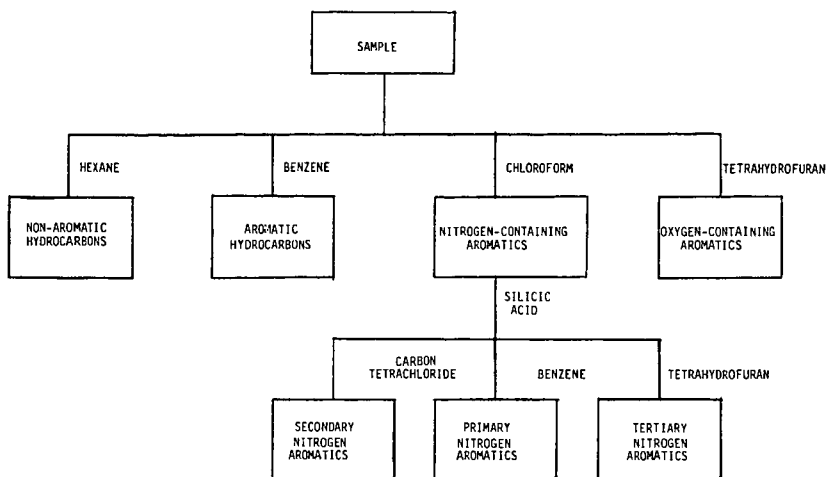


FIGURE 1. METHOD FOR SEPARATION OF FRACTIONS INTO CHEMICAL CLASSES BY COLUMN CHROMATOGRAPHY

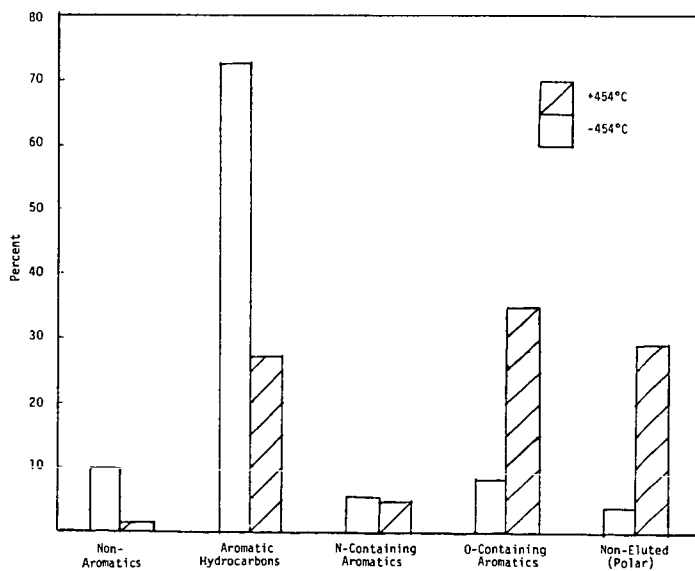


FIGURE 2. DISTRIBUTION OF CHEMICAL TYPES IN -454°C AND +454°C RECYCLE SOLVENT

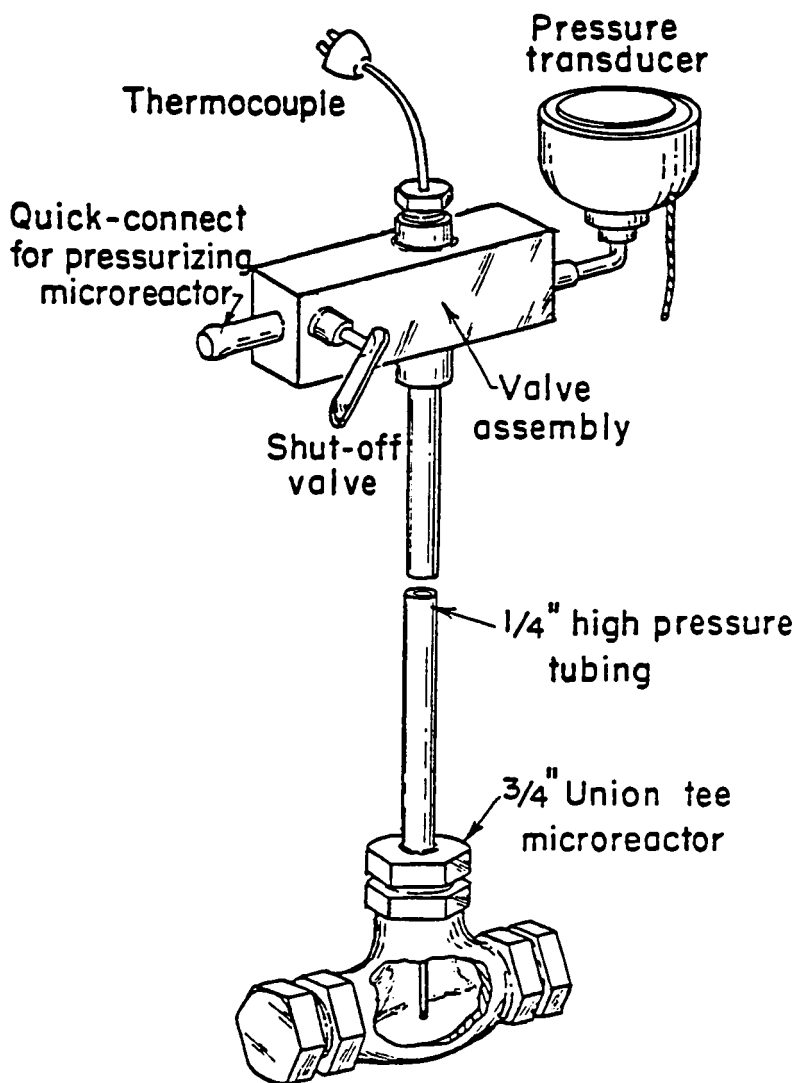


FIGURE 3. MICROAUTOCLAVE REACTOR